NASA-TM-112336

INTERSTELLAR ICES, THEIR PROCESSING, AND THEIR RELATIONSHIP TO REFRACTORY DUST

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ABSTRACT This paper reviews the existing spectral evidence that interstellar dense molecular clouds contain mixed molecular ices consisting of, among other things, H_2O, CO, CH_3OH, CO_2, and a CN-containing component. An understanding of the ices in dense molecular clouds is important, not only because they represent a major reservoir of material in these environments, but also because it is thought that they play an important role in the production of additional molecular materials that cannot be made via normal gas phase processes. For instance, the production of H_2 is thought to occur on icy grain mantles and dust grains. Also, laboratory studies of interstellar ice analogs containing the molecules listed above have demonstrated that radiation processing of the ices produces a number of new molecular components including (but not restricted to) CO, CO_2, HCO, H_2CO, and CH_4. When these processed ices are warmed to higher temperatures the various components of the ice recombine resulting in the production of refractory organic residues. Evidence for the existence of refractory residues of this type in space has recently been obtained.

INTRODUCTION

Icy materials constitute a significant fraction of the elemental inventory of most dense molecular clouds (cf. Tielens and Allamandola 1987). Thanks in large part to the development of sophisticated infrared observational instruments and to complementary laboratory studies, our understanding of these ices has progressed substantially in recent years. Our knowledge of the composition of interstellar ice is largely based on infrared spectra obtained using embedded objects within the clouds as sources against which the transmittance properties of the intervening dust are measured. The embedded object (often a protostar) heats nearby dust which then re-emits the energy at infrared wavelengths. As the infrared radiation passes through the cloud, molecules along the line-of-sight absorb photons at their fundamental frequencies. The flux distribution emerging from the cloud then shows absorption features diagnostic of the cloud material. An example of the spectra obtained in this way is given in Figure 1.

Because the grains in dense molecular clouds are cold (typically 10-50 K), most gaseous atoms, radicals, and molecules stick to the grains, and the solid

state column density of most species exceeds their gas phase column density (cf. Allamandola 1984; Tielens and Allamandola 1987; and references therein). Chemical reactions not possible in the gas phase can occur between reactive components on grain surfaces. As a result, the composition of the ice will not just reflect the local gas composition, but can also include other species formed directly on the grains. Theoretical attempts to integrate gas and grain chemistry into a single model indicate that icy grain mantles produced in this way should fall into two categories defined by the gas phase H/H_2 ratio (Tielens and Hagen 1982; d'Hendecourt et al. 1986; Brown 1988; Williams 1988). If this ratio is large, reactions with H atoms are important and simple hydrides dominate the ice. If the H/H_2 ratio is substantially less than one, reactive species such as O and N may react and form less reduced species. Thus, two qualitatively different categories of mantle could be produced by grain surface reactions, one
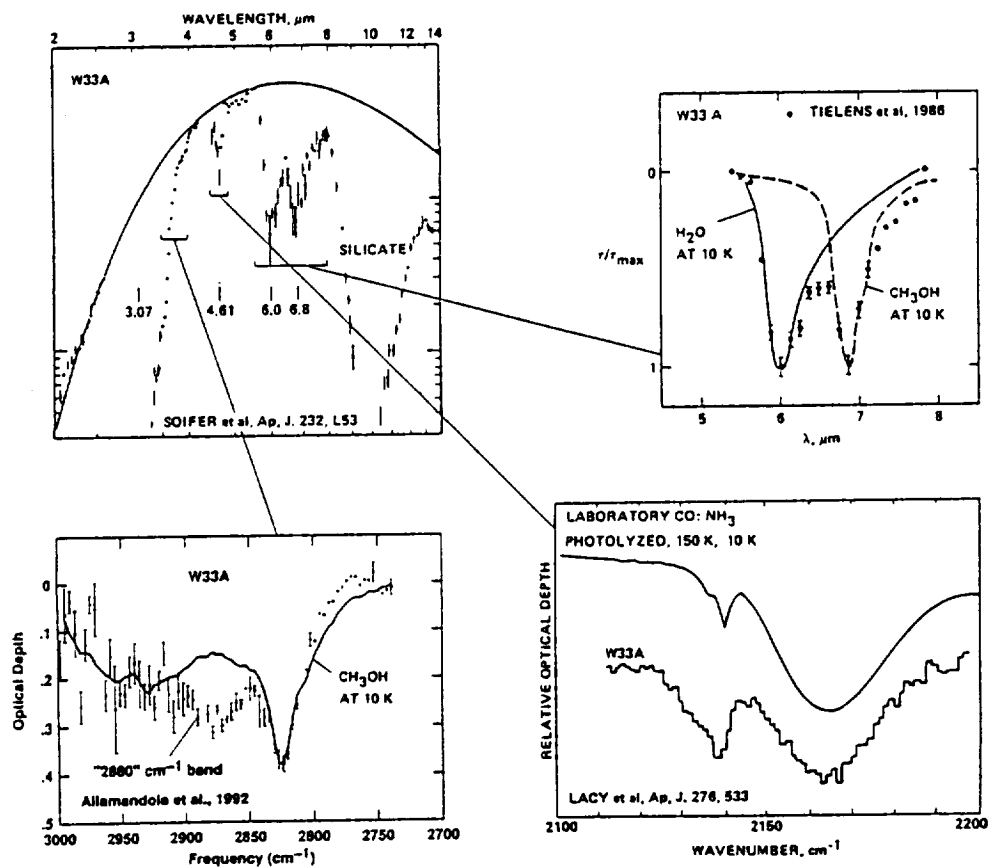

Fig. 1 The spectrum of W33A. The insets include spectra of (a) the entire mid-infrared spectrum, (b) the 5-8 μm region showing bands due to H_2O and CH_3OH, (c) the C-H stretching region showing bands due to CH_3OH and "micro-diamonds", and (d) the bands due to solid state CO and X(CN) (insets adapted from the listed references).

characterized by polar, H-bonded molecules and the other characterized by non-polar or only slightly polar, unsaturated molecules. These two types of ices are expected to be important in different zones within clouds.

New species can also be produced by the energetic processing of the ice mantles by ionizing radiation. Many laboratory studies have demonstrated that the processing of interstellar ices by charged particles (cf. Moore and Donn 1982; Strazzulla et al. 1983; Lanzerotti et al. 1985) and ultraviolet photons (cf. Hagen et al. 1979; d'Hendecourt et al. 1986; Allamandola et al. 1988) produces a wide variety of new molecular species, some considerably more complex and refractory than the original components in the ice. Finally, Schutte et al. (1993) have recently shown that formaldehyde in ices can react at very low temperatures and result in the production of new complex species.

DISCUSSION

Here I will review the present evidence for the existence in the interstellar medium of the types of ice and organic products discussed above. This evidence is based on both the astronomical infrared data and the results of appropriate laboratory studies. For clarity, the discussion will be organized into sections, each of which deals with a specific molecular component of the ice.

Water (H_2O) and Silicates
The first (and strongest) infrared absorption bands to be detected in the spectra of embedded protostars were features peaking at ~ 3250, 1670, and 1000 cm^{-1} (3.1, 6.0, and 10 μm) due to the O-H stretching and H-O-H bending modes of H_2O ices, and the Si-O stretching vibration of silicates, respectively (see Fig. 1). While these materials are important constituents of dense molecular clouds (H_2O is generally the most abundance ice component present, having column densities of 10^{18} - 10^{19} molecules/cm^2), they have both been extensively discussed elsewhere (cf. Knacke and Kratschmer 1980; Hagen et al. 1981; Leger et al. 1983) and so will not be discussed further here.

Carbon Monoxide (CO)
The fundamental C≡O stretching vibration of CO near 2140 cm^{-1} (4.67 μm) was first tentatively identified in dense molecular clouds in the spectrum of W33A by Soifer et al. (1979). Lacy et al. (1984) demonstrated that the CO was present in the solid state and the band has since been detected towards a large number of (but not all) embedded objects (cf. Whittet et al. 1985; Eiroa and Hodapp 1988; Tielens et al. 1991; Kerr, this book). When detected, the CO abundance is typically 1-5% that of the solid H_2O. The lower right inset in Figure 1 shows the solid state CO band in the spectrum of W33A. The exact position, width, and profile of the band is found to vary from source to source, but the overall feature can generally be described as the superposition of a narrow (FWHM of ~ 5 cm^{-1}) band centered near 2140 cm^{-1} (4.67 μm) and a broader (FWHM of ~ 10 cm^{-1}) band centered near 2136 cm^{-1} (4.68 μm). The relative strength of these two components varies substantially from object to object, although the narrower feature is usually the stronger of the two.

Laboratory experiments show that the position, width, and profile of the solid state CO feature depends on the composition, temperature, and history of the ice matrix in which the CO is frozen (Sandford et al. 1988). The broader CO spectral component is well fit by CO frozen in a polar matrix dominated by H_2O, which is not surprising since H_2O is the most abundant ice molecule in the clouds. However, the work of Sandford et al. (1988) show that the narrow component at 2140 cm^{-1} cannot be fit by CO intimately mixed with H_2O or any other polar mantle species thought to be important in molecular clouds. The peak position and width can be best matched by CO frozen in non-polar matrices (but not pure CO). Figure 2 shows a comparison between the narrow 2140 cm^{-1} interstellar CO band and a CO_2:CO ice at 10 K. Other non-polar matrices such as O_2 or N_2 may also provide a good fit to the narrower CO band component. A final identification of the non-polar matrix material has yet to be made and will probably require careful use of optical constants in conjunction with theoretical modelling that takes into account the effect of grain sizes and shapes on the band profiles. For an excellent treatment of the theoretical modelling of these effects for CO ices see Tielens et al. (1991). An extensive compilation of appropriate optical constants for CO and other ices relevant to astrophysics can be found in Hudgins et al. (1993).

The detection of the two components of the solid CO provides evidence for chemical heterogeneity of the ices along the line-of-sight and represents the first evidence for the existence of icy mantles dominated by species other than H_2O. The presence of non-polar matrices is consistent with their predicted formation in cloud regions where the H/H_2 ratio is less than one and H-addition reactions on grain mantle surfaces no longer dominate the gas-grain chemistry.
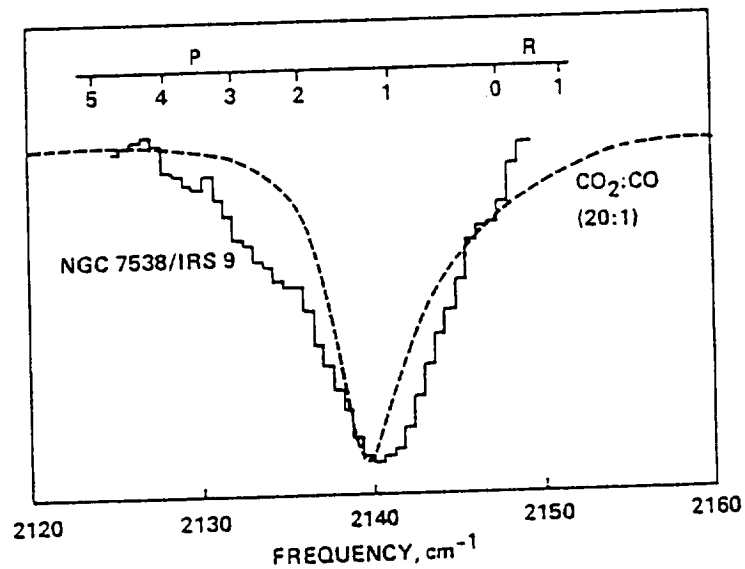

Fig. 2 A comparison of the CO band profile in the spectrum of NGC 7538 IRS9 and a laboratory CO_2:CO = 20:1 ice. The position and profile of the interstellar CO feature demonstrate that most of the CO is frozen in a non-polar (i.e. non-H_2O dominated) matrix (adapted from Sandford et al. 1988).

Component X(CN)

To date, a broad feature near 2160 cm⁻¹ (4.63 μm) has been observed in the spectra of three obscured objects, namely W33A and NGC 7538 IRS9 (Lacy et al. 1984) and L1551 IRS5 (Tegler et al. 1993). The depth of this feature does not correlate with the other bands in the infrared spectrum, indicating an independent carrier phase. The band in W33A can be seen in the lower right inset in Figure 1. This feature is generally attributed to a CN stretching vibration, although the exact identity of the carrier remains in doubt [hence the notation X(CN)]. Lacy et al. (1984) attributed the band to a nitrile (-C≡N) or isonitrile (C≡N-) containing material. This identification has been questioned by Grim and Greenberg (1987), who suggested the OCN⁻ ion may be the carrier.

While the CO band indicates that gas-grain surface chemistry can account for much of the chemical nature of interstellar grain mantles, the X(CN) band suggests that other processes are also at work. Unpublished laboratory studies by van de Bult in 1982 and 1983 showed that the 2160 cm⁻¹ feature could be produced by UV irradiation of ices containing C and N. Some of this work is described in Lacy et al. (1984). Recent laboratory work shows that the UV photolysis of ices having compositions like those of molecular clouds invariably produce a feature that matches the observed interstellar band (Allamandola et al. 1988; Tegler et al. 1993). The feature remains present even when the samples are warmed above 200 K, at which time all the original ice components have sublimed away and only an organic residue remains. This indicates that the interstellar carrier may be a relatively refractory material, a point inconsistent with the OCN- ion identification. In any event, the good agreement between the interstellar spectra and the lab spectra of photolyzed ices suggests that a CN-containing material is present in interstellar grains in some clouds and that some form of energetic processing is responsible for its production.

Methanol (CH₃OH)

Determination of the presence (or absence) of methanol in interstellar ices is of great importance since this molecule can have profound effects on the physical and photolytic properties of the overall ice (Allamandola et al. 1988; Blake et al. 1991). Until recently, the suspicion that CH₃OH was present in interstellar ices was based entirely on the presence of a broad 1460 cm⁻¹ (6.85 μm) absorption band in the spectra of many embedded objects (cf. Tielens et al. 1984; Tielens and Allamandola 1987) (Fig. 1 - upper right inset). The feature in W33A is well fit by the spectrum of CH₃OH in H₂O. If this identification is correct the abundance of CH₃OH in the ices can be quite high (up to and exceeding 50% that of H₂O). Gas phase chemistry models cannot explain such large abundances of methanol, although the CH₃OH may be made by gas-grain H atom addition reactions on CO (see the contribution by Bohn et al., this book).

In the past year a number of new observations have confirmed the methanol identification through the detection of additional absorption features. These include an overtone/combination band pair at 2600 and 2540 cm⁻¹ (3.85 and 3.94 μm) (Allamandola et al. 1992), and a C-H stretching vibration at 2825 cm⁻¹ (3.54 μm) (Grim et al. 1991; Allamandola et al. 1992; Fig. 1 - lower left inset). In terms of the total number of vibrational modes detected,

methanol is now better identified in the ices than is H_2O, so there can presently be no doubt that methanol is a major component of many interstellar ices.

Ammonia (NH_3)

NH_3 should be present in many interstellar ices as it is abundant in the gas phase and will certainly stick to grains at temperatures of 10-50 K. It has been suggested that some of the substructure seen in the O-H stretching band of interstellar H_2O ice might be due to the presence of solid state NH_3 (Hagen et al. 1980; Knacke et al. 1982). However, this structure can also be explained by grain size-dependent scattering effects (Smith et al. (1989). Thus, to date there has been no definitive identification of NH_3 in interstellar ices.

Carbon Dioxide (CO_2)

CO_2 is expected to be a significant component of interstellar ices, both because it can be produced in the gas phase in some interstellar environments (cf. d'Hendecourt et al. 1985) and because it is made during the photolysis of virtually any ice containing C and O atoms (cf. Allamandola et al. 1988). Unfortunately, the absorption bands of interstellar CO_2 ices are difficult to observe from Earth due to interference from telluric CO_2. Searches for interstellar CO_2 will require either the detection of weaker overtone/combination bands or the use of spaceborne instruments. In the latter regard, it should be noted that d'Hendecourt and Jourdain de Muizon (1989) suggest that frozen CO_2 is responsible for an absorption band seen in some IRAS LRS spectra of embedded protostars. They deduce a concentration of ~1% that of the solid H_2O. The advent of new spaceborne telescopes like ISO and SIRTF should greatly expand our knowledge of the distribution of CO_2 in interstellar ices.

Other Components

The spectrum of W33A also shows a weak band near 2040 cm^{-1} (4.90 μm) thought to be associated with ice mantles (Geballe et al. 1985; Larsen et al. 1985). Identifications proposed include an unspecified S-containing organic compound, CH_3OH, and the radicals C_3 and CN. The position of this band is also close to that observed for the CO stretch in OCS (Hudgins et al.1993).

It should be noted that, while methanol is now known to be responsible for most or all of the 1460 cm^{-1} (6.85 μm) absorption in objects like W33A and NGC 7538 IRS9, this feature is much broader and more complex in the spectra of other objects. In these cases methanol cannot explain the entire feature and other carriers must be present. Suggestions for other materials that could contribute to the absorption in this spectral region include carbonates and silicates (Knacke and Kratschmer 1980; Sandford and Walker 1985; Hecht et al. 1986), the NH_4+ ion (Grim et al. 1989), and organics such as ketones (e.g., acetone: CH_3COCH_3) or aldehydes (e.g., formaldehyde: H_2CO).

Refractory Organic Residues

There have been many studies of the production of organic materials by the processing of ices by ionizing radiation (cf. Hagen et al. 1979; Moore and Donn 1982; d'Hendecourt et al. 1986; Allamandola et al. 1988). In general, the carbon in these experiments has been provided by CH_4. In the last reference, however, the majority of the C was introduced in the form of CH_3OH. In view

of the recent verification that methanol is a major component in many interstellar ices, the results reported in Allamandola et al. (1988) are particularly relevant to interstellar ices and their photolysis products. They found that UV processing of CH_3OH-containing ices resulted in the production of HCO, H_2CO, CO_2, CO, CH_4, and an X(CN) component, largely at the expense of the photolytic disruption of CH_3OH. Subsequent warming of these ices produced a relatively refractory residue containing a number of different components. Similar or identical components might be expected to survive on interstellar grains when they are ejected from dense molecule clouds into the diffuse interstellar medium. Indeed, the C-H stretching absorption of dust in the diffuse ISM is very similar to that of the residues produced in this way (Sandford et al. 1991; Pendleton et al. 1993; Pendleton, this book). Very recently, a new feature centered near 2880 cm-1 (3.47 μm) has been discovered in the spectra of a number of dense molecular clouds (Fig. 1 - lower left inset). The position of this feature is highly characteristic of tertiary carbon and it has been taken as evidence for the presence of a diamond-like carbon component containing between 5 and 15% of the carbon in these clouds (Allamandola et al. 1992).

Abundances
The column density of an ice molecule or molecular subgroup can only be accurately determined for species in which individual band strengths have been measured in the solid state in the appropriate matrix. The column density of a solid state molecule can be estimated using techniques described elsewhere (cf. d'Hendecourt and Allamandola 1986; Hudgins et al. 1993). Space limitations preclude a complete discussion here and the interested reader is referred elsewhere for more complete treatments of ice phase abundances in dense molecular clouds (cf. Tielens and Allamandola 1987; Allamandola and Sandford 1988). It is important to remember that the derived values represent the total material along the entire line-of-sight. As was discussed in the section on CO, it is quite possible, perhaps even likely, that the local relative proportions of these materials may vary substantially along the line-of-sight.

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